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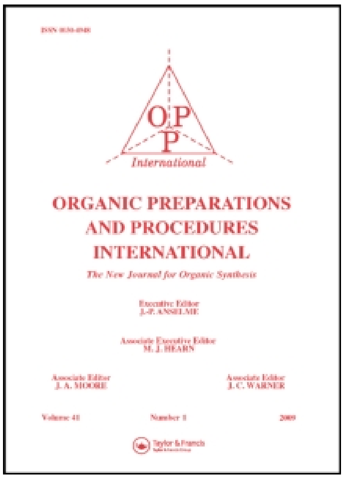

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# SULFATED ZIRCONIA AS AN EFFICIENT CATALYST FOR TETRAHYDRO PYRANYLATION AND ACETALIZATION‡

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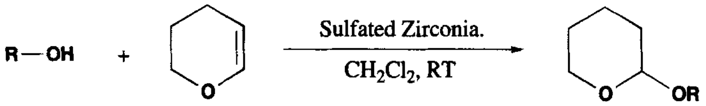
In recent years, there has been considerable growth in interest in the catalysis of organic reactions by solid superacid catalysts as they are potential alternatives to other strong acids that have been targeted as environmentally undesirable.[1] Of the several solid superacid catalysts, sulfated zirconia ($SO_4^{2-}/ZrO_2$) exhibits highest acid strength ($H_0 \leq -16.04$).[2-4] It can be prepared easily by a sulfate treatment of zirconium hydroxide followed by calcination. Sulfated zirconia has been found to be a useful catalyst in a variety of reactions such as the skeletal isomerization of butanes and pentanes,[4] the acylation of aromatics with acetic and benzoic acids,[4] synthesis of esters,[5] the condensation of hydroquinone with aniline,[6] the dehydration of carboxamides to nitriles,[7] the alkylation of *o*-xylene with styrene[8] and the alkylation of phenol by $C_9$ and $C_{12}$ olefins.[9] We now report usefulness of sulfated zirconia catalyst in tetrahydropyranylation of alcohols and phenols and acetalization of carbonyl compounds.

**Tetrahydropyranylation of alcohols and phenols**

The tetrahydropyranyl (THP) group is one of the most frequently used groups to protect alcohols and phenols.[10] Owing to the outstanding stability of THP ether under a variety of reaction conditions such as in basic media. reduction with hydrides, Grignard, lithium alkyls, oxidative, alkylating and acylating reagents, 3,4-dihydro-2H-pyran is still a reagent of choice for protection of the alcohol group in peptide, nucleotide and carbohydrate chemistry.[11]



Treatment of a variety of alcohols and phenols with 3,4-dihydro-2H-pyran in dichloromethane at room temperature, in the presence of a catalytic amount of sulfated zirconia gave the corresponding THP-ethers in high yields (**Table 1**). The reaction conditions are particularly mild and work-up procedure involves a filtration, followed by chromatography. Sulfated zirconia is recovered and reactivated for reuse by calcinating at 650°. The present procedure for preparation of THP-ether is quite general as a wide range of hydroxyl containing compounds such as primary, secondary, tertiary and allylic alcohols as well as phenols and naphthols may be protected. The use of a 20% excess THP with 2-chloroethanol increased the yield by 4%. It should be noted that the conventionally employed *p*-toluenesulfonic acid for tetrahydrapyranylation may be undesirable for highly acid-sensitive alcohols. In contrast, sulfated zirconia was very effective with allyl alcohol, propargyl alcohol and 2-methyl-2-propanol; isomerization of multiple bonds and dehydration of *tert*-butanol were not observed.

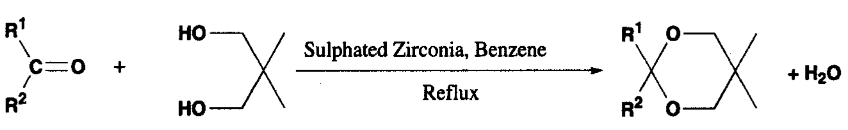
**TABLE 1.** Sulfated Zirconia-catalyzed Tetrahydropyranylation of Alcohols and Phenols

| Entry | Alcohol or Phenol | Time (hrs) | Yield (%) | mp. (°C) or bp. (°C)/Torr | lit. mp. (°C)or bp. (°C)/Torr |
|---|---|---|---|---|---|
| 1 | *n*-Hexanol | 1 | 96 | 125/25 | 94/3[21] |
| 2 | *iso*-Butanol | 1 | 90 | 84/25 | 80-85/25[22] |
| 3 | tert-Butanol | 1 | 94 | 55/15 | 54-58/13[22] |
| 4 | Cyclohexanol | 1 | 88 | 152/20 | 150-157/25[22] |
| 5 | Allyl alcohol | 1 | 85 | 75/25 | 75/22[23] |
| 6 | Propargyl alcohol | 1 | 89 | 81/25 | 76-79/25[22] |
| 7 | 2-Chloroethanol | 0.25 | 87 | 96/18 | 89-90/14[24] |
| 8 | Tetrahydrofurfuryl alcohol | 0.50 | 90 | 126/12 | 51/0.07[25] |
| 9 | Phenol | 0.25 | 92 | 103/4 | 90-92/3.5[26] |
| 10 | *p*-Cresol | 0.50 | 80 | 100/4 | 98-99/3[26] |
| 11 | 1-Naphthol | 5 | 88 | 39 | 38.5-39.6[27] |

Furthermore, this method is advantageous because of ease of isolation of the products in high yields and the recyclability of the catalyst.

### Acetalization of Carbonyl Compounds

Carbonyl group is one of the most versatile functional group in organic chemistry and a great deal of synthetic work has been performed on the protection of the carbonyl compounds as cyclic acetals.[10] The most convenient and practical methods for the synthesis of acetals from aldehydes and ketones are to react carbonyl compounds with diols in the presence of an appropriate acid catalyst with azeotropic removal of water formed.[12] A number of methods have been reported for the acetalization of carbonyl compounds with different catalysts.[13,19] Treatment of variety of aldehydes and ketones with 2,2-dimethyl, 1,3-propanediol in benzene at reflux temperature in the presence of a catalytic amount of sulfated zirconia afforded the corresponding acetals were obtained in high yields.



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a) $R^1$ = H, $R^2$ = 2-Furyl
b) $R^1$ = H, $R^2$ = $C_6H_5$
c) $R^1$ = H, $R^2$ = 4-Cl•$C_6H_4$
d) $R^1$ = H, $R^2$ = 2,4-$Cl_2C_6H_5$
e) $R^1$ = H, $R^2$ = 4-MeO•$C_6H_4$
f) $R^1$ = H, $R^2$ = 3-MeO, 4-$OHC_6H_3$
g) $R^1$ = H, $R^2$ = 2-$NO_2$•$C_6H_4$
h) $R^1$ = H, $R^2$ = 3-$NO_2$•$C_6H_4$
i) $R^1$ = H, $R^2$ = 4-$NO_2C_6H_4$
j) $R^1$ = H, $R^2$ = $C_6H_5CH{=}CH$
k) $R^1$ = $CH_3$, $R^2$ = $C_6H_5$
l) $R^1$ = $CH_3$, $R^2$ = 4-Cl•$C_6H_4$
m) Cyclopentyl
n) Cyclohexyl

The results are presented in **Table 2**. This procedure of acetalization appears to be quite general as both aldehydes and ketones were smoothly converted into acetals in excellent yields. The work up procedure is exceedingly simple and involves merely a filtration. Sulfated zirconia is recovered and reactivated for reuse by calcination at 650°.

**Table 2.** Sulfated Zirconia-catalyzed Acetalization of Carbonyl Compounds

| Compd | Reaction time (hrs) | Yield (%) | mp./bp. 760 mm Hg (°C) | $^1$H NMR ($\delta$ J,Hz) |
|---|---|---|---|---|
| **2a** | 3 | 88 | (235) | 0.78 (s, 3H, $CH_3$); 1.25 (s, 3H, $CH_3$); 3.65 (s, 4H, 2x$OCH_2$); 5.50 (s, 1H, Ar-CHO); 7.20(m, 3H, Ar-H) |
| **2b** | 6 | 93 | (240) | 0.80 (s.3H, $CH_3$); 1.28 (s, 3H, $CH_3$); 3.68 (s, 4H, 2x$OCH_2$); 5.60 (s, 1H, ArCHO); 7.10(m, SH, Ar-H) |
| **2c** | 3.5 | 98 | (237) | 0.80 (s, 3H, $CH_3$); 1.30 (s, 3H, $CH_3$); 3.70 (s, 4H, 2x$OCH_2$); 4.37 (s, 1H, Ar-CHO); 7.23(d, 2H, J = 4.5Hz, Ar-H); 7.70(d, 2H, J = 4.5Hz, Ar-H); |
| **2d** | 6 | 89 | (>250) | 0.70 (s, 3H, $CH_3$); 1.33 (s, 3H$CH_3$); 3.66 (s, 4H, 2x$OCH_2$); 5.53 (s, 1H, ArCHO); 7.43(m, 3H, AR-H) |
| **2e** | 11.5 | 95 | (60) | 0.77 (s, 3H, $CH_3$); 1.23 (s, 3H, $CH_3$); 3.60 (s, 4H, 2x$OCH_2$); 3.70 (s, 3H, $OCH_3$); 5.23 (s, 1H, ArCHO); 6.67 (d, 2H, J = 4Hz, Ar-H); 7.33(d, 2H, J = 4Hz, Ar-H) |
| **2f** | 30 | 94 | (80) | 0.77 (s, 3H, $CH_3$); 1.30 (s, 3H, $CH_3$); 3.67 (s, 4H, 2x$OCH_2$); 3.90 (s, 1H, $OCH_3$); 5.30 (s, 1H, ArCHO); 7.00(m, 3H, Ar-H) |
| **2g** | 2.5 | 92 | (163) | 0.80 (s, 3H, $CH_3$); 1.23 (s, 3H, $CH_3$); 3.70 (s, 4H, 2x$OCH_2$); 6.00 (s, 1H, ArCHO); 7.63(m, 4H, Ar-H) |
| **2h** | 3 | 65 | (120) | 0.79 (s, 3H$CH_3$); 1.30 (s, 3H, $CH_3$); 3.70 (s, 4H, 2x$OCH_2$); 5.37 (s, 1H, Ar-CHO); 7.55(m, 4H, Ar-H) |
| **2i** | 2.5 | 79 | (47*) | 0.80 (s, 3H, $CH_3$); 1.30 (s, 3H, $CH_3$); 3.70 (s, 4H, 2x$OCH_2$); 5.43 (s, 1H, ArCHO); 7.70(d, 2H, J = 4Hz, Ar-H); 8.20(d, 2H, J = 4Hz, Ar-H0 |
| **2j** | 4 | 97 | (43*) | 0.70 (s, 3H, $CH_3$); 1.22 (s, 3H, $CH_3$); 3.69 (s, 4H, 2x$OCH_2$); 4.90 (d, IH, J: 8Hz, ArCHO); 7.05 (dd, 1H, J = 16Hz and 8Hz = CH.CHO); 7.4 (d, 1H, J = 16Hz, A rCH = 7:5(m, SH, Ar-H |
| **2k** | 8.5 | 97 | (148) | 0.78 (s, 3H, $CH_3$); 1.25 (s, 3H, $CH_3$); 2.05 (s, 4H, ArC-$CH_3$); 3.65 (s, 4H, 2x$OCH_2$); 7.30 (m, 5H, Ar-H) |
| **21** | 6 | 99 | (120) | 0.78 (s, 3H, $CH_3$); 1.30 (s, 3H, $CH_3$); 2.00 (s, 3H, ArC-$CH_3$); 3.85 (s, 4H, 2x$OCH_2$); 7.35(d, 2H, J = 4Hz, Ar-H) |
| **2m** | 1.2 | 70 | (198) | 0.97 (s, 6H, 2x$CH_3$); 1.35 - 1.70(bs, SH, 2x$OCH_2$); 3.35 (s, 4H, 2x$OCH_2$) |
| **2n** | 4.2 | 85 | (162) | 0.91 (s, 6H, 2x$CH_3$); 1.33-1.75 (bs, 10H, 5 x$CH_2$); 3.33 (s, 4H, 2x$OCH_2$) |

## EXPERIMENTAL SECTION

Sulfated zirconia[20] was supplied by MEL Chemicals, U.K. and was calcinated at 650° in a furnace for 3 hrs, then cooled under nitrogen. This catalyst was then used directly for the reaction.

**Tetrahydropyranylation of Alcohols and Phenols. General Procedure.**- To a magnetically stirred mixture of the alcohol (12 mmol), dry dichloromethane (20 mL) and sulfated zirconia (100 mg), was added 3,4-dihydro-2H-pyran (12 mmol). The progress of reaction was monitored by TLC. Upon completion of the reaction, the mixture was filtered to remove the zirconia catalyst which was washed with dichloromethane (2 x 15 mL) and the combined flitrate and washings was evaporated. The residue was column chromato-graphed on a silica gel (60-120 mesh) with petroleum ether (60-80°) as eluent to afford the pure product. All the products were characterized by IR, $^1$H NMR and $^{13}$C NMR spectra.

**Acetalization of Carbonyl Compounds. General Procedure.**- A mixture of the carbonyl compound (10 mmol), 2,2-dimethyl-1,3-propanediol (10 mmol) and sulfated zirconia (100 mg) in benzene was stirred under reflux for the specified time (**Table 2**). The water formed was removed azeotropically. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and catalyst was washed with dich-loromethane (4 x 10 mL). The solvent was removed under reduced presure to afford product in high yield and in nearly pure form. All products were characterized by $^1$H NMR spectra.

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